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Alteration of stone materials on Sardinian medieval monuments:

physical, chemical and petrographic analysis for their restoration and preservation

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Abstract: Sardinian medieval monuments are mainly made up by volcanic rocks (pyroclastics/ignimbrites), minor granitoids and sedimentary rocks that show a more or less significant chemical-physical alteration. Mineral-petrographic features, physical properties related to petrogenetic processes, as well as manufacturing, strongly influence type and intensity of stone-decay.

The granitoids show an alteration degree less than the other rock-types, due to low porosity (<10%) that does not favor an easy absorption of circulating solutions, thus avoiding the water-rock interaction and hydrolysis. In a few cases, a physical intra-crystalline decohesion, that causes a rounding of the sharp edges of ashlars, can occur. The presence of oxidation patinas and the chloritization of micas are imputable to the action of chemical alteration phenomena.

The pyroclastics/ignimbritites, widely used in medieval architecture for the excellent workability, are affected by greater alteration due to the different mineral composition, mainly including glass (>70%), and physical features (higher porosity, 20-45%) due to a variable welding degree. Chemical alteration is not always evident since is more slow than the physical degradation (with macroscopic forms of pitting, exfoliation, alveolation).

The low porosity (<10%) limestones show a typical alteration which preferentially occurs on the outer surface of ashlars (with solubilization-reprecipitation processes), while sandstones and calcarenites (porosity >25%) generally show an advanced stages of decay, giving rise to physical macroscopic forms similar to those of the pyroclastic rocks. The chemical alteration preferentially acts on the carbonatic cement.

The paper makes a contribution to the preservation of Sardinian monuments, suggesting a new approach to define the different alteration-types of rocks in relation with their local exposure to the weather alteration phenomena. In particular, data on *i)* the changes of physical properties on surface of stone (porosity, water absorption, micro-morphology), acquired by laboratory tests and photogrammetry observations, *ii)* the newly-formed phases observed at the ashlars' surface (e.g., secondary minerals, soluble salts), by mineral (XRD) and chemical (XRF) investigations, will be reported and discussed.

Keywords: Medieval monuments, Mineralogic-petrographic features, Physical properties, Chemical-physical decay, Micro-photogrammetry

Introduction

Medieval churches of Sardinia (XI-XIV century) were built in Sardinia in a particular historical and geo-political context: at that time the territory was divided into different kingdoms, called Giudicati (DELOGU

1988; SERRA 1988). The skilled workers engaged for the construction of these monuments came from northern Italy to Tuscany, and generally realized external wall masonry at double curtain.

The external side of the ashlars, facing the façades, was worked in squared forms. The unworked parts of ashlars were placed toward the inside, to be not visible, and/or irregular ashlars placed inside the walls. This last feature possibly provided a better fit among the interspaces of ashlars, gradually filled during the construction, thus also giving a greater structural strength to the monument. The stone surfaces of the façades were seldom plastered (WINKLER 1994); therefore, sometimes the designer architect attempts the approach of different source materials and colors for obtaining bichromatic effects.

These purely aesthetic and stylistic choices, did not take into account the different physical-petrographic features of building materials. In this way, inappropriate materials having different physical-mechanical features were frequently wrongly used. Indeed, the alteration phenomena differently affect different geomaterials, each of which have an own specific resistance to physical and chemical attacks. Consequently, the effects of the decay are particularly manifest with the passing of time, especially where different lithotypes are juxtaposed (e.g., basalts and limestones).

Different rock-types were used in the construction of many Middle Ages Sardinian churches and basilicas (CORONEO 1993; COLUMBU et al. 2015), mainly magmatic and sedimentary rocks, largely spread in the island. Metamorphic rocks, as marls and gneiss, low available in the island, were minor used. The use of a lithotype in building is strongly related to the local availability of materials; therefore, constructions made up by rocks coming from far outcrops or outside of the island are uncommon. As is known, only structural and decorative elements (columns, capitals, frames, jambs, lintels) were built with rocks of outside provenance.

The effusive lithotypes (i.e., volcanic) are the most used building-rocks among the igneous-types. They were employed for the construction of many Romanic churches located in northern-central Sardinia (e.g., Sant'Antioco di Bisarcio, Santissima Trinità di Saccargia, San Pietro di Sorres, Santa Maria di Otti, San Demetrio and Santa Maria di Castro, Santa Maria del Regno), central Sardinia (e.g., San Nicola di Ottana, San Gregorio di Solarussa), southern Sardinia (e.g., San Geminiano di Samassi). The intrusive-types are less used and generally occur in Gallura, northern Sardinia (MURINEDDU 1962).

The volcanic rock-types were widely used in medieval architecture, even in earlier times, as Neolithic,Punic, Roman (ANTONELLI et al. 2014; COLUMBU et al. 2013; BERTORINO et al. 2002; MELIS & COLUMBU 1998) for the excellent workability. Although they are affected by greater alteration than other igneous lithotypes (COLUMBU et al. 2014a, b; COLUMBU et al. 2015; CORONEO & COLUMBU 2010; MACCIOTTA et al. 2001; YURTMES S. & ROWBOTHAM G. 1999), due to their low-medium degree of welding (COLUMBU et al. 2011), they show an adequate durability in time. It depends on both the intrinsic features of the material (chemical composition, physical properties), weathering and exposure condition.

Sedimentary rocks, widespread in whole Sardinia, were mainly used along with the volcanic lithotypes for the construction of the churches located in northern Sardinia (e.g., Santissima Trinità di Saccargia, San Pietro di Sorres, Santa Maria di Tergu, San Pietro del Crocifisso di Bulzi); only sedimentary rocks were used in the building of some churches located in western and southern Sardinia (e.g., Santa Giusta in the Oristano land, San Pantaleo di Dolianova, Sant'Efisio di Nora at Pula).

The results concerning the study of alteration processes affecting the main lithotypes used in the construction of Romanesque churches in Sardinia are here discussed. Four churches were selected as case-studies, since they are recognized as the most significant and representative of the Romanesque architecture in the island: San Simplicio di Olbia, S.S. Trinità di Saccargia di Codrongianos, San Nicola di Ottana, San Pantaleo di Dolianova (Fig. 1a, b, c, d).

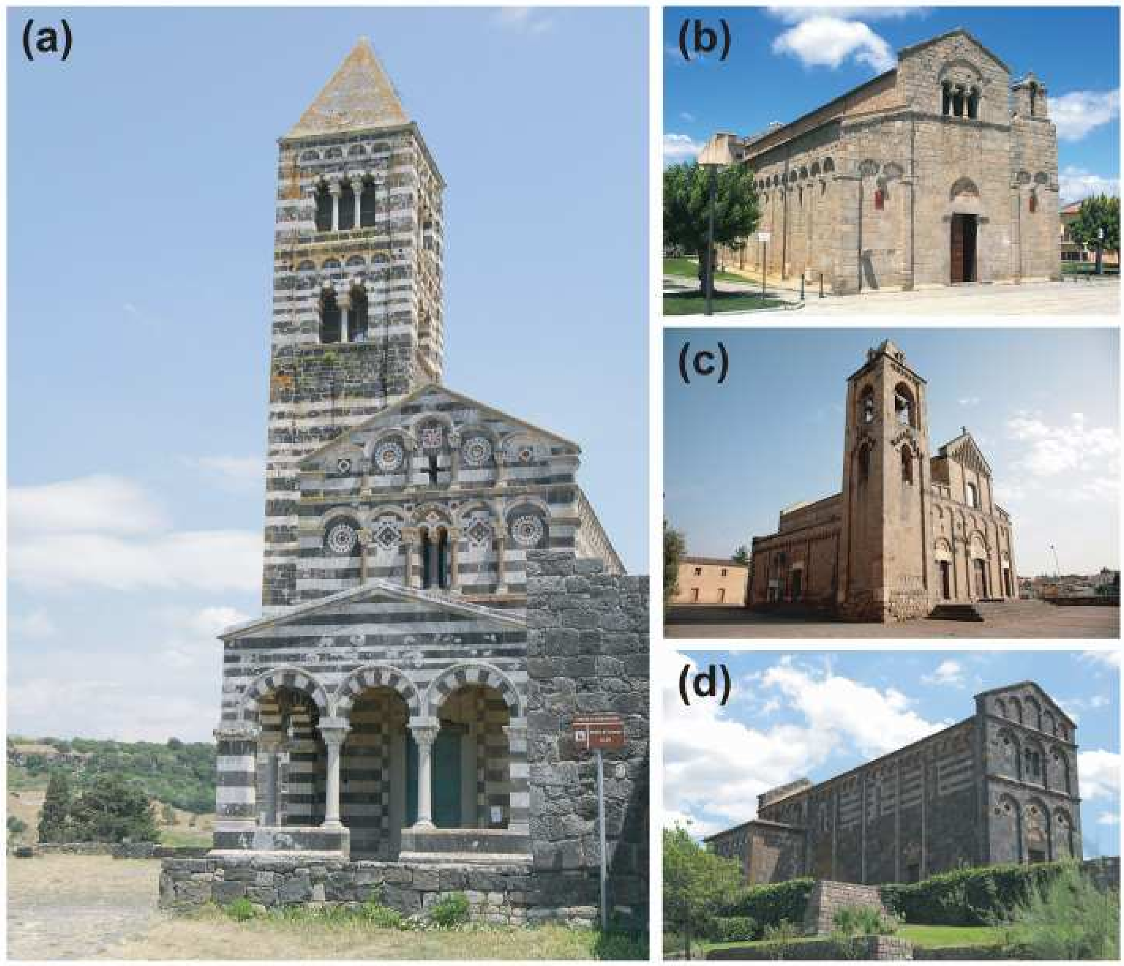

Fig. 1a, b, c, d – (a) Santissima Trinità di Saccargia church (Codrongianos, Sassari, North Sardinia); (b) San Simplicio church (Olbia, North-East Sardinia); (c) San Pantaleo church (Dolianova, South Sardinia); (d) San Nicola church (Ottana, central Sardinia).

Sampling and methods

A previously projected and planned thematic sampling of the construction materials in the previous cited churches, was carried out indoor and outdoor on the exposed faces of the monuments. Small rock fragments were collected in different parts of the masonry structures, more or less affected by alteration processes. Samples were geo-referenced and digitalized by a laser scan survey, scheduled, also annotating all significant macroscopic characteristics.

In areas strongly affected by degradation (presence of patinas, efflorescences, crusts, etc.), a micro-sampling of the newly-formed minerals and soluble salts, occurring as alterations on the natural stones and mortars, was also performed.

All samples were ground and homogenized to obtain powdered samples to analyze by different techniques. Petrographic determinations of mineral phases and textural studies were carried out on polished thin sections by optical polarised microscopy.

Mineral studies were performed on the bulk samples by the X-Ray Powder Diffraction (XRPD) analytical method. Data were collected by a Rigaku Geigerflex apparatus, equipped by a monochromator, using Cuk_α radiation, at 30 kV and 30 mA, filter Ni, from 3-70 °2ϑ, and step sampling 0.01 °2ϑ. Mineral identification was carried out by JADE 5.0 software, using the JCPDS Data Base (2010).

For physical tests, the specimens were dried at 105 ± 5°C and the dry solid mass (m_D) was determined. The solid phases volume (V_S) of powdered rock specimens (on 5-8 g and with particle size less than 0.063 mm) and the real volume (with $V_R = V_S + V_C$, where V_C is the volume of pores closed to helium) of the rock specimens were determined by a helium Ultrapycnometer 1000 (Quantachrome Instruments). The wet solid mass (m_W) of the samples was determined after water absorption by immersion for ten days. Through a hydrostatic analytical balance, the bulk volume V_B (with $V_B = V_S + V_O + V_C$, where $V_O = (V_B\text{-}V_R)$ is the volume of open pores to helium) is calculated as: $V_B = [(m_W\text{-}m_{HY})/\rho_w T_X]\bullet 100$

where m_{HY} is the hydrostatic mass of the wet specimen and $\rho_W T_X$ is the water density at a temperature T_X.

Total porosity (Φ_T), open porosity to water and helium ($\Phi_O H_2O$; $\Phi_O He$, respectively), closed porosity to water and helium ($\Phi_C H_2O$; $\Phi_C He$), bulk density (ρ_B), real density (ρ_R), solid density (ρ_S) were computed as:

$\Phi_T = [(V_B\text{-}V_S)/V_B]\bullet 100$; $\Phi_O H_2O = \square[(m_W\text{-}m_D)/\square_W T_X]/V_B\square\bullet 100$; $\Phi_O He = [(V_B\text{-}V_R)/V_B]\bullet 100$; $\Phi_C H_2O = \Phi_T$ - $\Phi_O H_2O$

$\Phi_C He = \Phi_T - \Phi_O He$; $\rho_S = m_D/V_S$; $\rho_R = m_D/V_R$; $\rho_B = m_D/V_B$

The weight imbibition coefficient (IC_W) and the saturation index (SI) were computed as:

$IC_W = [(m_W\text{-}m_D)/m_D]\bullet 100$; $SI = (\Phi_O H_2O/\Phi_O He) = \square[(m_W\text{-}m_D)/\ \rho_W T_X]/V_O\square\bullet 100$

The punching strength index was determined with a Point Load Tester (mod. D550 Controls Instrument) according to the International Society for Rock Mechanics (1972; 1985) on the same pseudo-cubic rock specimens used for other physical properties (Tab. 1). The load was exerted via the application of a concentrated load with two opposing conical punches. The resistance to puncturing (I_S) was calculated as P/D_e^2, where P is the breaking load and D_e is the "equivalent diameter of the carrot" (ISRM, 1985), with $D_e = 4A/\pi$ and $A = W\bullet D$, where W and 2L are the width perpendicular to the direction of the load and the length of the specimen, respectively. The index value is referred to a standard cylindrical specimen with diameter D = 50 mm for which I_S has been corrected with a shape coefficient (F) and calculated as:

$I_{S(50)} = I_S\bullet F = I_S\bullet(D_e/50)0.45$

Church	**Materials**	ρ_R (g/cm^3)	ρ_B (g/cm^3)	$\Phi_\square$ (%)	IC_W (%)	**SI (%)**	$I_{S(50)}$ (MPa)
SS. Trinità Saccargia	Basalt	2,85 ± 0,01	2,19 ± 0,06	27,38 ± 0,33	4,49	42,75 ± 7,14	3,69 ± 1,33
	Limestone	2,7 ± 0,03	2,2 ± 0,20	21,52 ± 3,04	6,91	83,59 ± 9,07	2,76 ± 1,14
San Simplicio	Granitoid rock	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Marble	2,73 ± 0,01	2,69 ± 0,33	4,24 ± 0,06	0,37	67,49 ± 14,99	2,93 ± 0,34
San Nicola	Ignimbrite	2,59 ± 0,33	1,92 ± 0,40	33,15 ± 10,04	13,99	87,05 ± 6,82	n.d.
San Pantaleo	Sandstone	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Marble	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

Table 1 – The main physical properties of building materials with mean values and standard deviation. Symbols legend: real density (ρ_R), bulk density (ρ_B), total porosity (Φ_T), water imbibition coefficient wt% (IC_W), water saturation index (SI).

Results

Mineral-petrographic characterization

Mineral composition and petrographic features of the six main rock-types making up four Romanic churches of Sardinia, along with associated alterations, were determined.

The *Basilica di Saccargia* (Codrongianos, North Sardinia), one of the most representative Romanesque churches in Sardinia was built by adopting an architectural solution given by alternating rows of basalt rocks and limestone blocks, to accomplish an artistic bichromatic effect (GIZZI 2007). The basalts, frequently used in this area as construction materials, occur in different facies characterized by closed porosity and sub-circular pores. Two principal facies, with different microscopic characteristics, can be distinguished: a) vesicular facies with fluidal texture, rare phenocrystals of olivine and plagioclase and holocrystalline ground-mass consists by microliths of plagioclase and clinopiroxene; b) facies with fluidal texture, oligoporphiric structure for rare phenocrystals of olivine and rare plagioclase, with holocrystalline ground-mass. According to mixed classification system (by microscopic analysis and chemical classification) the composition vary from trachy-andesitic to trachybasalt.

XRPD analysis of alteration crusts of ashlars consist mainly of plagioclases (belong to mineral assemblage of "basaltic" rocks) and occasionally K-feldspars (probably as xenocrystal from basement). Minor minerals, as mica and/or iron oxides, can locally occur. Newly-formed minerals, deriving from chemical alteration, can however locally occur and are mainly represented by the smectite-group minerals (generally montmorillonite) up to 10 wt%, and illite up to 5 wt%. Celadonite, glauconite, K-Ca-Mg sulfates, are occasionally detectable and generally occur in traces.

Two main limestone rocks were recognized. The former is a biomicritic limestone (FOLK 1959), microscopically characterized by the presence of bioclasts (bivalves, echinoids, gastropods, planctonic micro-foraminifera and corals). Texture is grain-sustained (micritic mud <0,062mm). No stratification is present. Silty fraction and fossils, without preferential orientation, are typical of a deep sea sedimentation environment (like abyssal plain). The latter limestone-rock, used in the construction of the church, is a biolitite characterized by a massive presence of bioclasts (up to 60% vol.), almost entirely represented by bivalves in fragments. Texture is depositional, with bioclastic components close together, forming a skeletal frame whose pores are filled with fine-grained carbonate cement. The absence of silty fraction support the hypothesis of a low-deep and high-energy depositional environment.

XRPD data show that limestones' ashlars generally consist of main calcite, but dolomite and/or magnesian-calcite can also locally occur in different amount (up to 15 wt%). Minor amount of quartz were locally found (up to 10 wt%). Newly-formed minerals, from alteration of limestones, were detected and generally occur in minor amounts. The most common are gypsum, which can locally occur up to 10 wt%, and illite, up to 5 wt%.

The church of *San Simplicio* (Olbia, North-East Sardinia; AGUS 2009; SECHI 1992) was built up by ashlars of local granitoid rocks. Also some decorative elements of white marbles have been found, (probably from Alpi Apuane) used especially close to the ground and some squared lesene of wall. Monzogranites (the so-called *ghiandone*) are the most abundant granitoid rocks used in the construction. The typical pink color is due to the presence of potassium feldspars, ranging in this facies from 30 to 60 wt%. Another typical facies is given by the sub-equigranular and inequigranular monzogranites, holocrystalline rocks, with isotropic texture, similar paragenesis to that of *ghiandone*, but lacking in phenocrysts of K-feldspar, and inequigranularity less marked. Finally, a third granitoid-type, less used in monumental constructions, is the granodiorite (the so-called *pietra rinaggina*), holocrystalline and inequigranular, with isotropic texture.

XRPD data show that mineral assemblage mainly consists of quartz, K-feldspars and plagioclases, occurring in different proportions in the different granitoid facies. Minor minerals, as micas, were also locally detected. Newly-formed mineral associations drastically depend on the original parent rock composition. The most common detectable alteration minerals are chlorites and/or illite.

The church of *San Pantaleo* (Dolianova, South Sardinia) was mainly built by sandstone blocks of local origin, with rare inserts of other geomaterials, as microcrystalline white marble, not sourced in Sardinia. The main rock-types, which come from local outcrops whose origin is currently being analyzed), are sandstones, conglomerates, grain-supported conglomeratic sandstones, mainly consisting of silica concrete and quartz-feldspathic clasts. Echinids, planctonic foraminifera, gastropods, bivalves, and corals can locally occur. These sandstone' facies formed in marine environments, and are closely in relation with the first sedimentary Oligocene-Miocene cycle.

The microcrystalline white marble is used as fragments or smaller ashlars. They are frequently shapeless, generally positioned in the basal rows, close to the ground, and in some decorative elements coming from other historical periods (probably Roman). Possibly, they come from the Alpi Apuane. The calcite occurs in a typical micro-crystalline structure (about 97% vol.). The sporadic presence of accessory minerals (<2%) and Fe-oxides (<1%) was also observed.

XRPD data show that sandstones' mineral assemblage mainly consists of quartz, K-feldspar and plagioclases. Minor micas (biotite and/or muscovite), and iron oxides can also be locally detected. The calcarenites' facies show a similar mineral pattern for major minerals; in addition, a consistent, but variable, amount of carbonatic minerals (calcite, Mg-calcite and dolomite), ranging from 20 to 40 wt%, was determined. Marls' facies mineral association consists of the same phase detected in the above-mentioned facies. In addition, kaolinite, montmorillonite and illite, become part of the main paragenesis of the rock.

Alteration phenomena drastically affect these rocks, giving rise to abundant newly-formed minerals. The alteration assemblage mainly include calcium sulphates, principally gypsum up to 15 wt%, and minor goethite and glauconite.

The *San Nicola* church (Ottana, central Sardinia) is built up with ashlars of local ignimbrites, mainly rhydacitic composition. A wide variety of colours, from blackish to orange-pink, and shades of intermediate tonalities, is typical of these facies. The welding of the rock is variable; generally, the orange-pink lithotypes are less welded than the dark ones. The ignimbrites belong to the Oligocene-Miocene volcanic cycle of Sardinia (BECCALUVA et al. 1985; COLUMBU et al. 2011). Petrographic observations show the presence of high amount of lithics (SKIRIUS et al. 1991), ipoialine mesostasi and marked isotropic textures (Fig. 2a). Secondary phases, due to alteration processes, frequently occur, especially phyllosilicates, such as glauconite and celadonite and observed in thin section (Fig. 2b). These volcanic rocks show a texture isotropic, color index of 5 to 7, with porphiritic structure (IP = 18-23%) for phenocrysts of opaque (~2% of phenocrysts), clinopyroxene (~5%), amphiboles (i.e., green hornblende; <2%), plagioclase and quartz.

XRPD analysis highlights that minor minerals, as micas, can locally occur. In addition, the mineral assemblage everywhere includes an important glass fraction, ranging from 20 to 60-70 wt%.

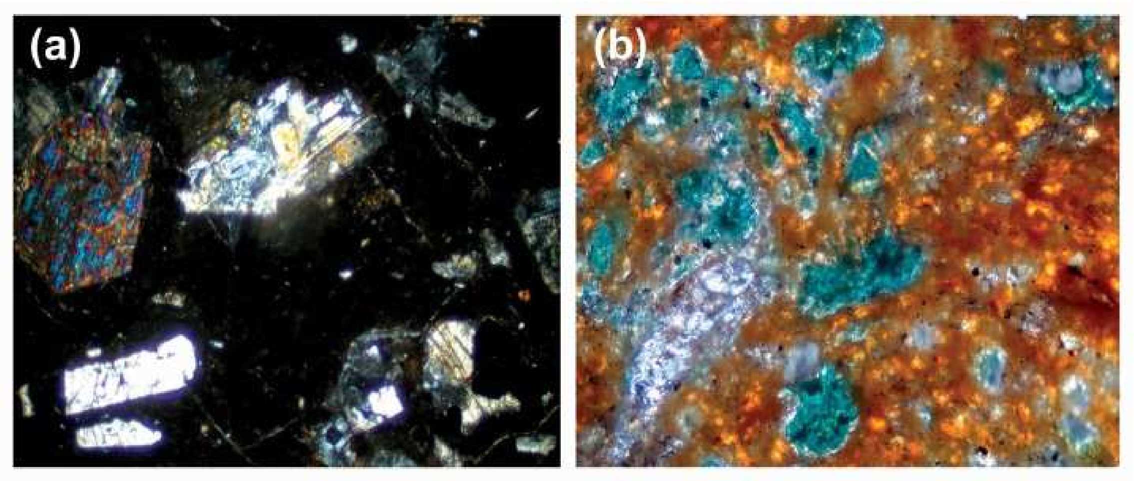

Fig. 2a, b – Micro-photographs on thin section under polaring microscope of ignimbrites from San Nicola church (Ottana, central Sardinia): (a) plagioclase and clinopyroxene crystals in black glassy matrix groundmass (crossed Nicol); (b) photo of glassy groundmass with green areas of alteration in celadonite and glauconite (parallel Nicol).

Physical properties of geomaterials

The two petro-genetically different rock-types, used in the construction of the *Basilica of Saccargia*, have physical features fully different. Values of real density vary from 2.85 g/cm^3 in basalts to 2.70 g/cm^3 in the calcareous rock-types (Tab. 1; Fig. 3a). No major differences, between basalts and limestones, were determined for bulk density, close to 2.20 g/cm^3 in both lithotypes, because the high real density of basalt (due to the presence of Fe-Mg-minerals) is compensated by its high total porosity (average 27.4%), whereas limestones have low real density and low porosity (< 21,5%). The absorption coefficients are markedly different between basalts (average 4.5% wt) and limestone rock-types (average 6.9 wt%), due to different distribution in two lithotypes of closed and open porosity to water. Also the mechanical properties are significantly different in the basalts and limestones.

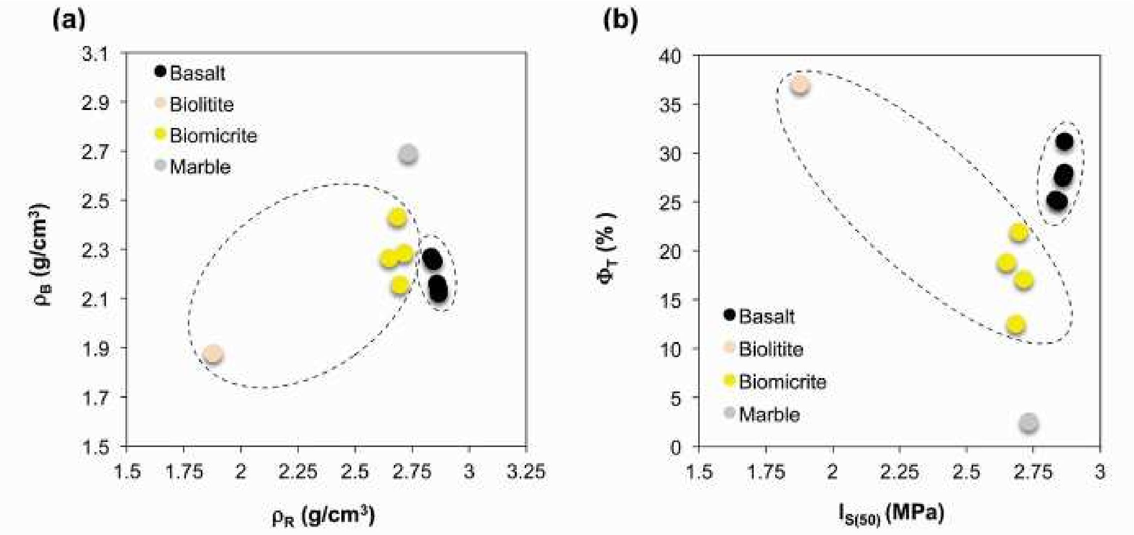

Fig. 3a, b – Comparison of some physical-mechanical properties between marble, limestones (biolitite, biomicrite) and basalts of Santissima Trinità di Saccargia church: (a) real density vs bulk density; (b) point load strength index vs total porosity; the different point load strenght index explains the differential erosion between the lithotypes.

The punching strength (normalized to a cylindrical sample, with a diameter of 50 mm; ISRM 1985) has average values I_{S50} = 3.69 MPa for basalts and 2.76 MPa for biolitites and biomicrites (Fig. 3b). The mechanical strength of a rock is usually closely related to the total porosity and to the resistance of the solid fraction. In this case, since when basalts and limestone have similar porosity but the punching strength is significantly higher in basalts, the resistance is principally due to the solid fraction of the material.

Physical properties of the ignimbrites of *San Nicola* church are quite different than those of basalts and other rocks analysed (Tab. 1). The real density, due to the presence of glass in the matrix, has an average value less than equal to 2.59 ± 0.33 g/cm^3. Due to different degrees of alteration and welding of the analysed samples, the bulk density and porosity show high variability with mean values of 1.92 ± 0.40 g/cm^3 and 33.15 ± 10.04%, respectively (Tab. 1; Fig. 4). During the test of absorption by immersion in water (useful in the calculation of the absorption coefficient) the blackish and orange ignimbritic lithotypes showed different behaviour. The pinkish-red colored rocks, less welded by decohesion, lost a greater mass than the black lithologies. The saturation index of ignimbritic lithotypes shows higher values than the other analyzed igneous rocks, with an average around 87% (Tab. 1).

The determination of the physical properties of the granitoid rocks of the church of *San Simplicio* and sandstones of *San Pantaleo*, is still in progress. Preliminary data acquired for the marbles of *San Simplicio* reveal that their features are similar to those determined for the marble from the Alpi Apuane found in other Romanesque monuments, although the porosity values evidence a greater degree of physical alteration.

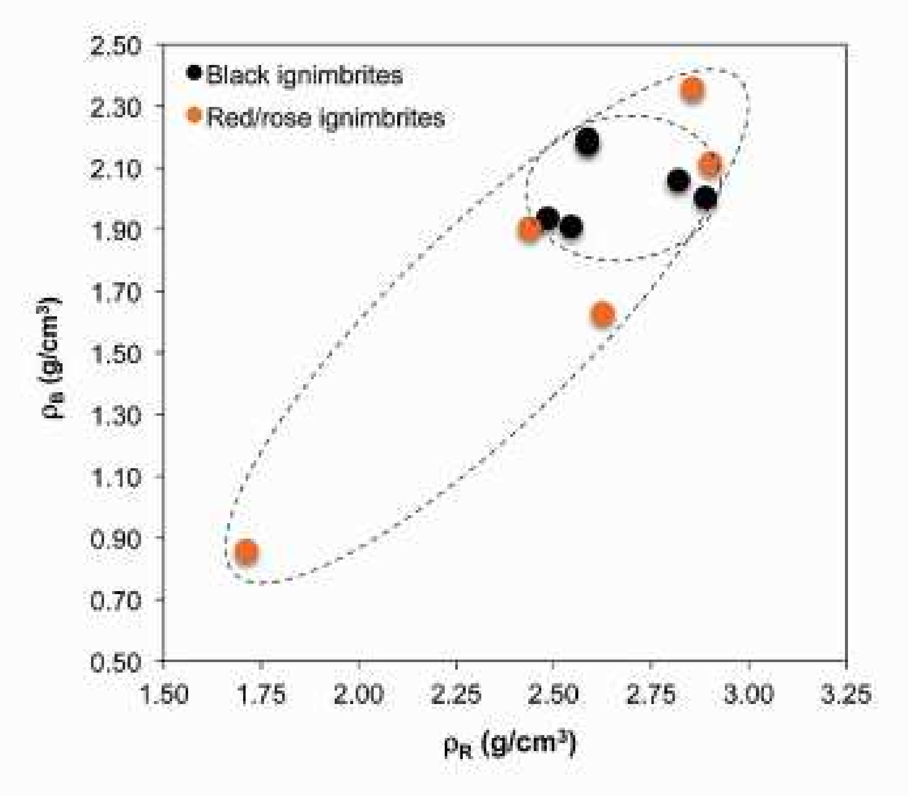

Fig. 4 – Real density *vs* bulk density of San Nicola ignimbrites divided in two populations according to their staining.

Discussion

Basilica di Saccargia church - The main macroscopic evidence between the basalt and the limestone ashlars is the differential alteration. Mechanical resistance (Tab. 1; Fig. 3b) is closely in relation with alteration, mineral composition and physical properties (density and porosity) of the rocks, strongly influencing welding and permeability, respectively. Thus, although basalts have higher porosity than the calcareous rock-types, the higher intra-matrix cohesion provides them a higher resistance to weathering and other physical actions. Limestones, although less porous than basalts, have a higher permeability, which favor and enhance dissolution processes, with consequent formation of alteration crusts, generally consisting of gypsum. Wash-out actions strongly abraded the surfaces, originating the concave curvature and the retraction of the vertical profile of the limestone ashlars; similar forms of erosion are not observed in the basalt ashlars.

Also mineral type, chemical composition and petrographic features strongly differ between limestones and basalts. That fact, strongly influencing the respective physical properties, is responsible of the differential alteration.

San Simplicio church - The granitoid rocks of the church of San Simplicio are principally subjected to physical degradation, which mainly favors the decohesion process of the quartz (MATIAS & ALVES 2002), K-feldspar and mica phases, due to the physical contact weaknesses among the different minerals (THURO & SCHOLZ 2003). Crystals forming the intrusive rock do not exhibit high values of porosity, but pores are still open favouring the fluid circulation. That cyclic action, in relation with the absorption/desorption of water, influences the internal stresses and the differential thermal expansion leads to a decohesion of the crystalline phases (Fig. 5b). Somewhere, the beginning of the formation of exfoliations and crusts can be observed in the external surfaces (BAHAT et al. 1999) can be observed. Rare chemical alteration products can be observed in some ashlars, possibly already altered in origin. XRPD analysis shows that newly-formed mineral association drastically depends on the original parent rock composition. The mineralogical changes mainly concern the partial/total transformation of biotites in chlorites (Fig. 5b) and plagioclases into kaolinite. The latter mineral, locally in association with Fe-hydroxides (goethite and gibbsite), and mixed-layer clays, occurs in minor amount. On the whole, the granitoids show an alteration degree less than the other studied rock-types, especially due to low porosity (<10%), which does not favour an easy absorption of circulating solutions.

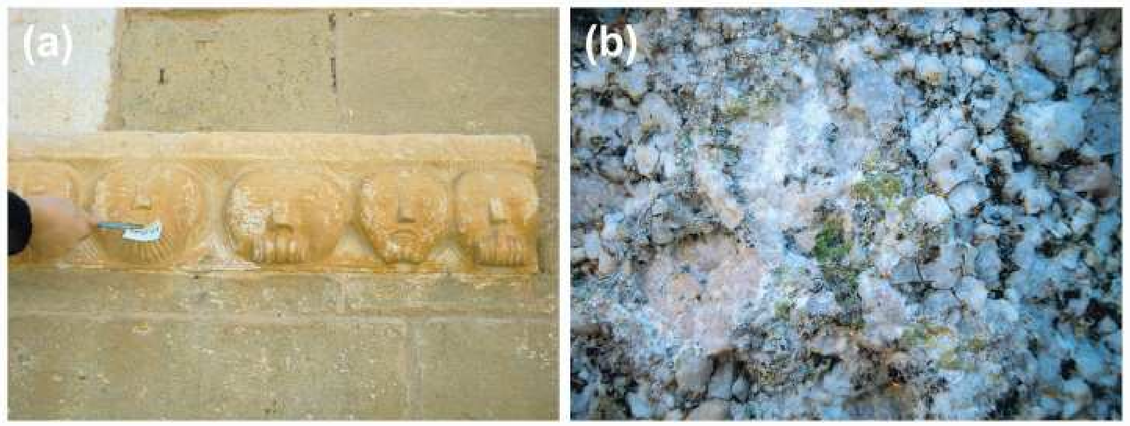

Fig. 5a, b – (a) Chromatic alteration on marbles surface (probably Ca-oxalate patina with typical ocher colour) of decorative elements of San Pantaleo Basilica (Dolianova, South Sardinia); (b) physical decohesion and disgregation on granitoid rock from San Simplicio church (Olbia, North-East Sardinia), where observing chloritization processes (green colour).

San Pantaleo church - The construction materials of San Pantaleo cathedral show that physical degradation processes are in relation with the silico-clastic sandstones, weakly cemented (FITZNER 1988). Indeed, the partial dissolution of siliceous cement favors the decay of the rock matrix. The dissolution can be caused by aggressive water or by mechanical processes, as shearing stresses initially acting along the stratification planes. Rounded quartz-clasts and their smooth surface enhance the dissolution process.
Also processes of exfoliation on the outer surfaces, mainly due to thermo-clastic tensions, are observed in the sandstone ashlars. The daily temperature gradients on the ashlars' surfaces can be very high, and consequent stresses can origin flaking. Exfoliation is also caused by the compression overload -induced produced by fractures, sub-parallel to the facade (BRADLEY 1963). Biological degradation dramatically affects the north-exposed rocks and those occurring in zones where ascents of capillarity is constant. In this areas, especially located in the rows of basal blocks, patinas of mosses and/or lichens dramatically affect the rock, spoiling its aesthetics and integrity. Also chemical alteration phenomena significantly affect these rock-types, in particular the carbonatic cement, giving rise to the formation of many newly-formed minerals (principally calcium sulphates, goethite and glauconite). On the whole, these rock-types are affected by advanced stages of decay due to the largely variable mineral/chemical composition and physical features. The marbles used as waste material (e.g., frames of the doors and windows), and belong to other historical periods, show a significant chemical alteration and consequent formation of calcium oxalate films (Fig. 5a), which chromatically modifies the wall surface. The presence of oxalates films can be attributed to previous restorations, and caused by treatments with organic substances (TIANO & PARDINI 2004). In conclusion, chemical or microbiological processes can favor the formation of oxalic acid, and the large abundance of calcium in marbles favours the formation of calcium oxalate.

San Nicola church - The ignimbrites of San Nicola di Ottana church (central Sardinia), widely used in medieval architecture for the excellent workability, are generally affected by physical decay (decohesion, exfoliation, alveolation, etc.; PEREZ RODRIGUEZ 2003). Pyroclastic rocks are generally affected by greater alteration than the other investigated lithotypes. That is due to the largely variable mineral/chemical composition, mainly including glass, as well as to the peculiar physical features. Newly-formed minerals form an important fraction of these rock-types since they are greatly affected by chemical alteration processes. XRPD data of alteration patina samples analysed show the presence of zeolites (mainly clinoptilolite and/or mordenite), as product of devitrification of volcanic glass. Smectite-group minerals (mainly montmorillonite), up to 30 wt%, almost everywhere occur; illite, up to 10 wt%, is present as secondary phases of alteration; celadonite and/or glauconite, generally occur in traces and are not common phases.

Conclusions

The methodological approach here proposed for the study of the physical-chemical features of construction materials can be considered the first important step in view of a possible restoration and conservation of any historical artifact.
For the achievement the final objective, i.e. the planning of adequate restoration/conservative strategies, after the preliminary phases (architectural relief and acquisition of historical data), fundamental phases for

assessing the decay intensity and determining the criticalities of the artifacts are: *i)* the macroscopic semi-quantitative assessment of the decay forms, *ii)* the planning of an adequate and targeted sampling, and *iii)* the application of diagnostic quantitative chemical-physical-mechanical methodologies. It should be noted that the application of different analytical methodologies and laboratory tests should be performed in relation to the specific issues. So, in addition to the analysis here presented and discussed, to solve other specific issues, data can be integrated by the application of the following analytical methodologies: XRF (X-Ray Fluorescence), to determine chemical composition, thermal (thermo-gravimetric and thermo-differential (TG-DTA)), e.g. for identifying nature of amorphous components and/or poorly crystalline phases, IC (Ion Chromatography), for determining soluble salts, SEM (Scanning Electron Microscopy), for defining microstructure and qualitative composition of single mineral phases, Micro FTIR (Fourier Transform Infrared Spectroscopy), for recognizing the presence of previously applied restoring products (acrylic, siliconic, etc), as their presence can negatively affect behavior and effectiveness of new products

Restoration and conservation phases will have therefore take into account the most important features and criticalities typical of the different construction materials, as well as the environmental conditions of the areas in which the monument is located. Indeed, the results of the investigations reported on this paper highlight the extreme variability of the state of conservation of different geomaterials, in function of their nature and local exposure.

As concerns specific results of this work, the investigations carried out on the most common stone materials, used for the construction of the Romanesque churches of Sardinia, have highlighted their physical-chemical features, as well as alteration features, the most common alteration products, the response of each lithotype to alteration phenomena attacks. The acquired information have been significant and fundamental in the determination of the mineral composition, micro-textural features and physical properties, content of soluble salts and porosity of the building materials.

Summarizing, among the different rocks, igneous rocks (i.e., granitoid rocks and basalts) are the building materials more resistant to chemical and physical decay. The low degree of alteration of granitoid rocks is due to the low porosity (<10%) that inhibits the circulation of solutions and, consequently, the water-rock interaction and hydrolysis. Traces of oxidation and chloritization processes of micas are the typical alteration products of this rock-type. Basalts show a high resistance to chemical and physical decay, although they show variable porosity and some mafic minerals can be affected by alteration (e.g., olivine that transforms into iddingsite). Only in some cases, local physical decay, due to thermal differential expansion, can observed at the ashlars' surface. The pyroclastic rocks, the most common used in Romanic architecture, show different alteration-types, depending on the presence of more or less amount of glass and variation in welding, original characteristics of the rocks. The latter factor affects the density and the bulk porosity (usually ranging from 20 and 50% vol.), affecting their durability. Physical decay occurs in several forms of macroscopic alteration: pitting, exfoliation, alveolation, fissuring. Occasionally, the ashlar located in the basal zone of the monument where samples show greater porosity, patinas of soluble salts can occur on the surface. Although limestones have low porosity (average <15%), chemical and physical alteration phenomena can be observed at the surface of ashlars (e.g., solubilization and re-precipitation of salts and surface erosion).

The critical analysis of the entire dataset, also implemented with data being acquired, will consent, in a later phase, to obtain a mapping of the material features and the decay forms, by a graphic representation, e.g. on thematic atlas suitably drawn for each single monument. In addition, the dataset will provide the base for an adequate planning in view of the application of optimal recovery actions to applied to the different monuments. The local critical weathering conditions, as well as the features of similar materials to use in the phase of restoration, will have also to be taken into account and accurately assessed, by environmental monitoring and the application of specific diagnostic chemical-physical-mechanical methodologies, respectively.

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